

Ethylene Polymers, LLDPE

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2. Molecular Structure and Properties

2.1. Comonomer Type and Content

Although practically any α -olefin from C_3 to C_{20} can be used as comonomer for LLDPE, the four most commonly used are 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Approximately 40% of LLDPE made uses 1-hexene as comonomer, approximately 35% uses 1-butene, and approximately 25% uses 1-octene. Only a small fraction is made using 4-methyl-1-pentene. Hexene and butene copolymers are more prevalent because they are less expensive than octene and because they are commonly used in the gas-phase process, which accounts for most of the global LLDPE production. For LLDPE, density is strongly controlled by comonomer content. Conventional LLDPE basically covers the density range of 0.915–0.940. Within that density range, and also lower density ranges, there are common product family subsets. Table 1 shows comonomer content and subsequent density ranges for commercial LLDPE.

Table 1. Comonomer Content and Density Ranges for Commercial LLDPE Resins

Family	Common name	Comonomer, mol%	Crystallinity, %	Density, g/cm ³
Medium density	MDPE	1–2	55–45	0.940–0.926
Low density	LLDPE	2.5–3.5	45–30	0.925–0.915
Very low/ultra low density	VLDPE/ULDPE	>4	<30	<0.915
Very low density (single-site catalyzed)	Plastomer	≤25	0–30	≤0.912

2.2. Chain Structure

LLDPE comprises linear molecules of ethylene and α -olefins and can be generally represented by the formula $!CH_2 !CH_2 !CH_2 !CH !(C_{n-2}H_{2(n-2)+1})$, where n is the number of carbon atoms in the α -olefin.

In LLDPE above 0.915 g/cm^3 density, most of the branching due to comonomer is randomly distributed along the polymer backbone, although there may be some adjacent comonomer units. Single-site-catalyzed resins have comonomer much more uniformly distributed along the polymer backbone than do conventional LLDPE resins. A conventional gas-phase hexene copolymer LLDPE at 0.918 g/cm^3 density has approximately 18 branches per thousand carbon atoms while a single-site-catalyzed gas-phase hexene copolymer LLDPE at the same density has 11–12 branches per thousand carbon atoms. In the single-site-catalyzed resins, the hexene is more randomly distributed along the backbone, shortening the average backbone sequence length for crystallization, and therefore less comonomer is needed to achieve the same density.

Most LLDPE chains have at least one methyl group at one chain end. Other chain ends can be a methyl group from termination from chain transfer, or a vinyl group or vinylidene group from termination from β -hydride transfer (1).

Generally speaking, LLDPE resins do not contain long-chain branching. However, certain families of plastomers may contain more than 0.01 long-chain branches per thousand carbons (2).

2.3. Composition

A representative schematic of the structural differences between LDPE, LLDPE, and single-site-catalyzed LLDPE is given in Figure 1.

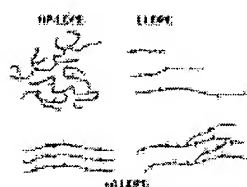


Figure 1. Structural differences between LDPE, LLDPE, and single-site-catalyzed LLDPE. [Full View]

LDPE contains a mixture of long-chain branching and short-chain branching. LLDPE contains only short-chain branching, but that branching is not uniformly distributed through the molecular weight. LLDPE made using Ziegler–Natta catalysts tends to have more comonomer in the lower molecular weight fraction and less in the high molecular weight fraction (3, 4). A temperature rising elution fractionation (TREF) plot for LDPE at 0.919 g/cm^3 and LLDPE at 0.918 g/cm^3 is shown in Figure 2.

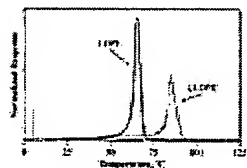


Figure 2. LDPE and LLDPE TREF comparison. [Full View]

As you can see, the peak elution temperature for the LDPE is much lower and the peak is much narrower than that for the LLDPE. This indicates that the LLDPE is more compositionally heterogeneous than the LDPE.

The first commercially available single-site-catalyzed polyethylenes were very low density resins called plastomers (5, 6), which had high levels of comonomer and were very homogeneous. Later, commercial commodity grade mLLDPEs were not quite as homogeneous as the plastomers, but were

still more homogeneous than LLDPE (7-9). Figure 3 shows a TREF plot of an LLDPE at 0.918 g/cm³ density and an mLLDPE at 0.917 g/cm³ density, both produced in the gas phase. Also included is a plastomer at 0.900 g/cm³ density produced in a slurry reactor.

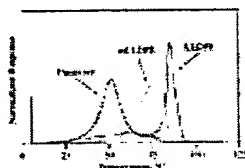


Figure 3. TREF profiles for LLDPE, mLLDPE, and plastomer.
[Full View]

A polymer that has branching more uniformly distributed along the polymer backbone will have shorter sequence lengths for polymer crystallization. Shorter sequence lengths result in thinner crystals that dissolve and elute at lower temperatures than thicker crystals. The mLLDPE has a lower peak elution temperature than LLDPE at the same density, indicating that mLLDPE is more compositionally homogeneous. The plastomer has a peak elution temperature of approximately 50°C and a very narrow peak indicating that the resin is very compositionally homogeneous.

2.4. Molecular Weight

Commercially available LLDPE resins can have weight-average molecular weights from less than 20,000 to over 200,000. *Melt index*, a measure of polymer flow through a specified die for a given time, is often used as an estimator of polymer molecular weight and is inversely proportional to weight-average molecular weight. An approximate correlation of weight-average molecular weight and melt index for LLDPE is shown in Figure 4.

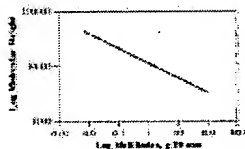


Figure 4. Molecular weight/melt index correlation for LLDPE.
[Full View]

Over the range shown, the relationship between molecular weight and melt index is linear but will not be completely linear over a broader range. Commercially available film grade LLDPE resins can range from 0.2 g/10 min to over 5 g/10 min melt index. Injection-molding grades vary in melt index from approximately 10 g/10 min to greater than 125 g/10 min. Table 2 shows measured molecular weights and melt-flow properties for several LDPEs and plastomers at nominal 1 g/10 min melt index.

Table 2. Melt Index and Molecular Weight Data for LDPE and Several LLDPEs

Property	HP-LDPE	Gas-phase LLDPE	Gas-phase mLLDPE	Plastomer	
				Slurry Solution	
Melt index I_2 ,	1.0	1.0	1.0	1.1	1.0

g/10 min					
MIR I_{21}/I_2	60	33	17	21	31
M_n , g/mol	22,000	28,000	44,000	46,000	40,000
M_w , g/mol	104,000	107,000	102,000	99,000	82,000
PDI, M_w/M_n	4.7	3.8	2.3	2.2	2.1

Molecular weight distribution plots for the resins in Table 2 are given in Figures 5 and 6.

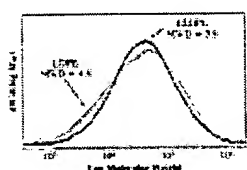


Figure 5. Molecular weight distribution plots for LDPE and LLDPE.
[Full View]

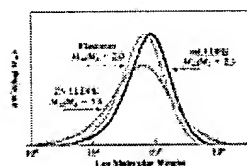


Figure 6. Molecular weight distribution plots for LLDPE, mLLDPE, and a plastomer.
[Full View]

Depending on the standards used for calibration of the molecular weight fractionation technique, LLDPE has a molecular weight polydispersity index (PDI, M_w/M_n) between 3 and 4.5 with melt index ratios (MIR, I_{21}/I_2) of 20–35. LDPE has PDI usually greater than 5 and contains long-chain branching. Therefore, although the LDPE and LLDPE resins shown have similar weight-average molecular weights and melt indices, their MIR (I_{21}/I_2) values are significantly different. The higher MIR for LDPE indicates greater sensitivity to shear caused by the broader PDI and long-chain branching.

The single-site-catalyzed mLLDPE and slurry plastomers have much narrower molecular weight distributions and therefore have much lower MIR values than LLDPE. The plastomer produced in solution phase has trace levels of long-chain branching that make it more sensitive to shear, giving it a higher MIR than the linear plastomer. A narrower PDI for the single-site-catalyzed resins means a smaller low molecular weight fraction commonly called hexane extractables, which can be a limiting factor for LLDPE use in food contact applications.

There is a relatively small volume of LLDPE resins made using chrome-based catalysts that have much broader PDI, 10 and higher, and MIR values of 70 and higher. Chrome-based LLDPEs are mostly used in wire and cable coatings, blow molding, and some film applications.

2.5. Chemical Properties

LLDPE is a saturated hydrocarbon and is generally unreactive. The most reactive parts of the polymer molecule are tertiary carbons at short-chain branch points and double bonds at chain ends. LLDPE is stable in alcohols, alkaline solutions, and saline solutions. It is not attacked by weak organic or

inorganic acids. Reactions with concentrated sulfuric acid (H_2SO_4 , >70%) at elevated temperatures can result in the formation of sulfo-compounds. LLDPE can be nitrated with concentrated nitric acid (HNO_3). Fuming nitric acid is also used in analytical techniques to etch away amorphous polyethylene. At room temperature, LLDPE is not soluble in low molecular weight solvent although very low molecular weight and very low density fractions may be extracted. At higher temperatures, LLDPE can be dissolved in certain aromatic, aliphatic, and halogenated hydrocarbons including xylenes, tetralin, decalin, and chlorobenzenes.

2.6. Physical Properties

All polyethylene above 0.86 g/cm^3 density is semicrystalline. The basic crystalline structure for most commercial LLDPE is chain-folded lamellae (Fig. 7). The body of the crystal consists of polymer backbone segments, and the surfaces are a collection of chain folds, loose cilia, and tie chains (chains incorporated into more than one crystal). When crystallized isothermally, it has been found that 95% of the lamellae in a given sample are within 5% of the same thickness (10). There is some debate over the mechanism of chain folding and of the subsequent fold loops. The most likely model includes adjacent reentry, loose adjacent reentry, and nonadjacent reentry. Short-chain branch length plays an important role in determining backbone flexibility for chain folding and subsequently fold loop size. Longer short-chain branches sterically hinder chain folding and therefore cause longer fold loops and increased numbers of tie chains. It has been found that a minimum sequence length of 14 carbons is needed for ready incorporation into a crystal lattice (11). The most stable crystalline form for polyethylene is orthorhombic with unit cell dimensions of $a = 7.42 \text{ \AA}$, $b = 4.94 \text{ \AA}$, and $c = 2.55 \text{ \AA}$. Research has shown that the chain axis is inclined at an angle of $30\text{--}45^\circ$ to the crystal surface (12, 13).



Figure 7. Schematic of chain-folded lamellar structure.
[Full View]

From very dilute solution ($\leq 0.1\%$ weight or volume) single, lozenge-shaped crystals are formed (Fig. 8). They have similar relative dimensions as a sheet of paper, Angstroms thick and microns in lateral dimensions. Cooled from an unstressed melt, LLDPE forms spherulitic structures, also shown in Figure 8. Spherulites form from a defect or nucleation site and are essentially ribbon-like lamellae radiating out from a central point. They begin as sheaf-like structures and grow into spherical shapes. Regions between lamellae are amorphous chain segments and tie chains (14, 15). The tie chain density between lamellae plays a dominant role in determining mechanical properties.



Figure 8. Single crystal and spherulitic structures.
[Full View]

It is now widely accepted that LLDPE will form row nucleated, a.k.a. “shish-kebob”, structures when crystallized in a melt subjected to a deviatoric stress, such as film extrusion (16-21). As given in Figure 9, a core of linear higher density polymer forms in the direction of stress (machine direction in film applications), and lamellae grow radially. Space between lamellae is filled with amorphous chain segments and tie chains. Some plastomers below 0.89 g/cm^3 density will form a fringed micellar morphology because of the very short backbone sequence length between branch points (22, 23).

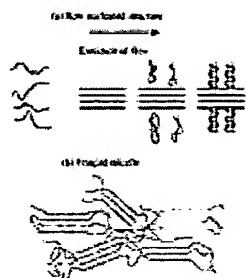


Figure 9. (a) Row nucleated and (b) fringed micelle structures.
[Full View]

Polymer crystals are rarely perfect and can include chain ends, voids, and at times short-chain branches. As it is generally concluded that the ethyl branch from butene comonomers can be incorporated into the crystal lattice (24-28), this may explain why longer comonomers give LLDPEs with improved properties. Hexene and octene comonomers are more likely to produce large fold loops or tie chains that improve toughness. Quick quenching from the melt also provides less perfect crystals and may allow longer branches to be included in the crystal lattice (29).

As mentioned earlier, LLDPE has a heterogeneous composition and a higher density fraction with minimal branching. Because of this higher density fraction and its thicker crystals, the maximum melting peak in the relatively broad melting range of LLDPE usually falls between 122 and 128°C and is somewhat independent of comonomer-type. Even nonuniform VLDPE resins can have a melting point above 120°C. LDPE has thinner crystalline lamellae than LLDPE and therefore has a lower melting point as shown in the differential scanning calorimetry (dsc) profiles in Figure 10. Homopolymer LDPE usually has a melting point between 105 and 115°C.

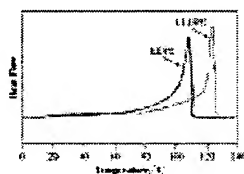


Figure 10. The dsc melting profiles for LDPE and LLDPE.
[Full View]

Because of its lower melting point, LDPE has been preferred over LLDPE for many heat-sealing applications. mLLDPE and plastomers are more compositionally homogeneous than LLDPE. Shorter backbone sequence lengths for crystallization results in thinner crystalline lamellae and therefore lower melting points (Fig. 11).

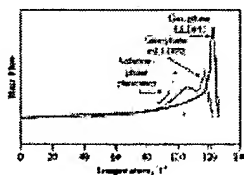


Figure 11. The dsc melting profiles for LLDPE, mLLDPE, and a plastomer.
[Full View]

mLLDPE produced in the gas phase and several produced in the slurry phase have peak melting points of 115–118°C. Plastomers have peak melting temperatures below 100°C. Lower melting points make single-site-catalyzed LLDPEs ideal for use as heat seal layers in many applications. Figure 12 shows heat seal strengths for LLDPE and mLLDPE, both at 0.917 g/cm³ density, and a 0.900 g/cm³ density

plastomer produced in a high pressure reactor. All have nominal 1 g/10 min melt index. The single-site-catalyzed resins have lower seal initiation temperatures and generally have higher hot tack strengths, which allows for shorter dwell time and faster line speeds.

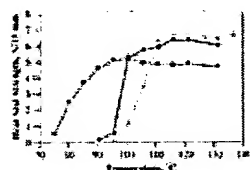


Figure 12. Heat seal strength comparison for LLDPE, mLLDPE, and plastomer. To convert N/15 mm to ppi, divide by 2.625. —○— LLDPE—; —◆— mLLDPE—; —△— Plastomer—. [Full View]

As with all polymers that are at least partially amorphous, polyethylene has a glass-transition temperature T_g where the transition from brittle solid to viscoelastic material occurs. There is still disagreement as to the actual T_g for polyethylene and researchers have proposed different temperatures of $-30 \pm 15^\circ\text{C}$ (30, 31), $-80 \pm 10^\circ\text{C}$ (32), and $-128 \pm 5^\circ\text{C}$ (33, 34). Above the melting point, polyethylene is a viscous liquid.

Polyethylene has a dielectric constant of 2.3 at 1 kHz which makes it suitable for use as wire and cable housing.

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